

QC-DMRG study of the ionic–neutral curve crossing of LiF

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We have studied the ionic–neutral curve crossing between the two lowest $^1\Sigma^+$ states of LiF in order to demonstrate the efficiency of the quantum chemistry version of the density matrix renormalization group method (QC-DMRG). We show that QC-DMRG is capable to calculate the ground and several low-lying excited state energies within the error margin set up in advance of the calculation, while with standard quantum chemical methods it is difficult to obtain a good approximation to Full CI property values at the point of the avoided crossing. We have calculated the dipole moment as a function of bond length, which in fact provides a smooth and continuous curve even close to the avoided crossing, in contrast to other standard numerical treatments.

I. INTRODUCTION

The development of the complete active space self-consistent field (CASSCF) method by Björn Roos' group [1] was a milestone in the development of electronic-structure methods effecting a rigorous treatment of electron correlation in molecules. In particular in the case of nearly degenerate states, i.e., in regions of the potential curve, where static correlation prevails, a CASSCF is almost indispensable for a good zero-order description of the electronic wave function, which usually is subsequently refined by methods like MRCI (multi-reference CI) or CASPT2 (second order perturbation theory based on a CAS reference state)[2, 3]. The latter methods focus on dynamic correlation and are mandatory for achieving quantitative agreement with experiment. A frequently studied test system for the quantitative calculation of electron correlation effects in molecules is the ionic–neutral avoided crossing in the potential curves of alkaline halogenides, in particular of LiF [4, 5, 6, 7, 8, 9, 10, 11, 12]. The goal of these benchmark studies is the development of a computational protocol which provides a globally accurate description of the system even though the wave functions change dramatically transversing the avoided crossing. New ab initio methods for the treatment of correlation should prove to provide a satisfactory description of the two states in question, and the present paper is devoted to the application of the quantum-chemistry density matrix renormalization group (QC-DMRG) to calculate the potential energy curve and the dipole-moment functions in the vicinity of the ionic–covalent avoided crossing in LiF.

Since its first application on the water molecule [13, 14] the QC-DMRG algorithm has become an alternative candidate to treat the electron–electron correlation in atoms and molecules in a rigorous way. The method has already been applied successfully to calculate the ground state

energy of various molecules containing up to 57 orbitals [15, 16, 17], demonstrating the capability of the method to provide the Full-CI results. The general trend of the accuracy of the first and second excited states calculated by the method and its strong connection to the structure of the reduced subsystem density matrix has also been studied in detail on molecules with various fraction of filling and orbitals [17]. Although results of DMRG calculations seem promising, it is still an open question to determine the stability and performance of the new method for systems in which the wave function character changes as a function of bond length, especially in the region of an avoided crossing.

In order to provide a benchmark test of the QC-DMRG algorithm for an ionic–neutral potential curve crossing, we have calculated the two lowest $^1\Sigma^+$ states of LiF. This system has been subject of various earlier theoretical studies [4, 5, 6]. Kahn, Hay and Shavitt [4] calculated the four lowest $^1\Sigma^+$ states using the configuration-interaction (CI) methods. The dipole moment function for the lowest $^1\Sigma^+$ states was studied by Werner and Meyer [6] using MCSCF wave functions. The remaining discrepancy between their results and the empirical estimate of Grice and Herschbach [18] was finally resolved by Bauschlicher and Langhoff who have employed full configuration interaction calculations to define a protocol using an MRCI approach based on carefully constructed CASSCF orbitals, which was found to satisfactorily represent the FCI potential and dipole moment curves for the two lowest $^1\Sigma^+$ states of LiF. Problems encountered in the application of CASPT2 [7, 8] have been recently resolved on occasion of the development of multi-state CASPT2 [11, 12].

Our aim in this paper is to assess the stability of the QC-DMRG method in the region of an avoided crossing and show that QC-DMRG provides the FCI energy within an error set up in advance of the calculation for all bond lengths. Taking the dipole moment as an example, we present a general QC-DMRG procedure to obtain expectation values of first order-properties for the ground and excited states in molecules using the DMRG method. To the best of our knowledge, this is the first time that excited-state data and properties have been calculated

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for a molecule in the framework of *ab initio* QC-DMRG.

The setup of the paper is as follows. In Sec. II we briefly describe the main steps of DMRG and the details of the numerical procedure used to determine the appropriate ordering and target state. Sec. III contains the numerical results and analysis of the observed trends of the numerical error. The summary of our conclusions is presented in Sec. IV.

II. NUMERICAL PROCEDURE

Detailed description of the DMRG algorithm can be found in the original papers [19, 20, 21, 22] and its application in the context of quantum chemistry is summarized in three recently published papers [15, 16, 17]. Therefore, we present only the most important formulas and definitions that are relevant to the question of current interest.

A. Hamilton operator

In the context of quantum chemistry a one-dimensional chain that is studied by DMRG is built up from the molecular orbitals that were obtained, e.g., in a suitable mean-field or MCSCF calculation. The electron–electron correlation is taken into account by an iterative procedure that minimizes the Rayleigh quotient corresponding to the Hamiltonian describing the electronic structure of the molecule, given by

$$\mathcal{H} = \sum_{ij\sigma} T_{ij} c_{i\sigma}^\dagger c_{j\sigma} + \sum_{ijkl\sigma\sigma'} V_{ijkl} c_{i\sigma}^\dagger c_{j\sigma'}^\dagger c_{k\sigma'} c_{l\sigma} \quad (1)$$

and thus determines the full CI wavefunction. In Eq. (1), T_{ij} denotes the matrix elements between orthogonal molecular orbitals $\{\phi_i\}$ of the one-particle Hamiltonian comprising kinetic energy and the external electric field of the nuclei, while V_{ijkl} stands for the matrix elements of the electron repulsion operator and is defined as

$$V_{ijkl} = \int d^3x_1 d^3x_2 \phi_i^*(\vec{x}_1) \phi_j^*(\vec{x}_2) \frac{1}{|\vec{x}_1 - \vec{x}_2|} \phi_k(\vec{x}_2) \phi_l(\vec{x}_1). \quad (2)$$

B. Target state

The desired eigenstate of the Hamiltonian that one wants to calculate is called the *target state* in the context of DMRG. The representation of such state in the DMRG procedure is derived from an arrangement of molecular orbitals in a linear chain, which in turn is divided into smaller subsystems and the wave function of the molecule is built up from the linear combination of basis states representing these subsystems.

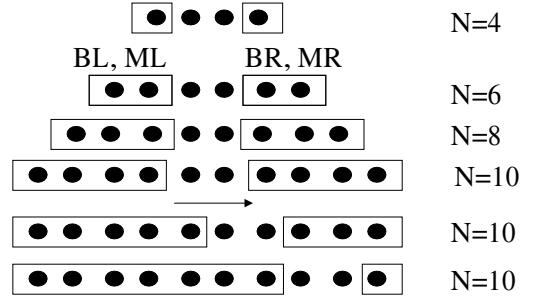


FIG. 1: The decomposition of the wavefunction to subsystems.

According to Fig. 1 the structure of the subsystems that is called *superblock* configuration is defined as $B_L \bullet \bullet B_R$, where B_L and B_R represents a block containing l and r molecular orbitals, respectively, and the \bullet denotes an orbital, in DMRG terminology a quantum site with q degrees of freedom. In our case q is equal to four, enumerating the doubly occupied, spin up, spin down and empty orbital situation. Since the number of molecular orbitals (N) is constant, it can be expressed as $l + r + 2 = N$. The B_L block is represented by M_L so-called renormalized block basis states ($M_L \leq q^l$), and each block state represents a special distribution of a given number of electrons with up and down spins on the l orbitals. The same holds for B_R with M_R block states.

In order to recover interactions of electrons in orbitals that are far away from each other in the chain and include their contribution to the correlation energy, the size of the left block is increased as long as $l \leq N - 3$ and the length of the right block is decreased so that $r + l + 2 = N$ always holds. This iterative procedure is repeated in the reverse way as well, until $r = N - 3$ and $l = 1$ as is shown in Fig. 1. This sweeping procedure implies that in each DMRG iteration step the Hamilton operator is constructed on a given superblock configuration and the wave function of the molecule is built up from the linear combination of the subsystem basis states with coefficients determined by diagonalizing the superblock Hamilton operator. If $|I\rangle$ and $|J\rangle$ denote basis states for $B_L \bullet$ and $\bullet B_R$ subsystems, respectively, then the β th eigenstate is written as

$$\Psi_\beta = \sum_{I,J}^{M_L * q, M_R * q} \psi_{I,J}^\beta |IJ\rangle, \quad |IJ\rangle = |I\rangle \otimes |J\rangle, \quad (3)$$

where $\psi_{I,J}^\beta$ is determined by diagonalization of the superblock Hamiltonian. In the simplest situation, the target state of the DMRG method that we want to calculate is one of the eigenstates of the Hamilton operator and can be usually determined with a good accuracy if the eigenstates are well separated.

As second key ingredient of the DMRG method is the selection of the block states for a subsequent iteration step. The $M_L^{\text{new}} \leq M_L * q$ block states are chosen from the eigenstates (ω_α) of the reduced density matrix of the

$B_L\bullet$ subsystem, that is constructed for the target state as

$$\rho_{I,I'}^\beta = \sum_J \psi_{I,J}^\beta \psi_{I',J}^\beta. \quad (4)$$

The error of the truncation procedure is measured by means of the deviation of the total weight of the selected states from unity which is defined as

$$TRE = 1 - \sum_{\alpha=1}^{M_L^{\text{new}}} \omega_\alpha. \quad (5)$$

As is was shown in Ref. 17 the accuracy of the DMRG calculation can be controlled by keeping the truncation error below a given threshold TRE_{max} and the number of block states above a minimum value M_{min} which avoids the iterative procedure being trapped by local attractors.

It is thus evident, that the construction of the target state has strong effect on the structure of the subsystem density matrix, on the block states used during all the subsequent iteration steps and on the converging properties of the DMRG method. If the target state does not contain those basis states that are important to represent the desired electronic configuration at a given bond length, the method can converge to a wrong state by losing the optimum structure of the target state. This has long been confirmed by various DMRG studies and the problem can be solved by constructing target states by coherent superposition of more eigenstates, in which case

$$\Psi_{\text{Target}} = \sum_{\beta} \omega_{\beta} \sum_{I,J}^{M_L * q, M_R * q} \psi_{I,J}^{\beta} |IJ\rangle. \quad (6)$$

The weights are usually taken as $\omega_{\beta} = 1$ for all β .

Another possibility to construct block states for the subsequent iteration step is first constructing the reduced subsystem density matrices for all eigenstates independently and then add them up, in which case the density matrix for an incoherent target states is defined as

$$\rho_{I,I'} = \sum_{\beta} \omega_{\beta} \sum_J \psi_{I,J}^{\beta} \psi_{I',J}^{\beta} \quad (7)$$

where again, $\omega_{\beta} = 1$ could be introduced. The construction of coherent or incoherent superpositions for targeting several excited states simultaneously is the the DMRG counterpart of the construction of averaged-states orbitals in a CASSCF calculation in order to obtain an optimal description of several many-particle states at the same time.

C. Identifying the energy levels

In the QC-DMRG algorithm block states representing a given number of electron with up and down spins are

identified with N_{up} and N_{down} quantum numbers. These are used in order to select out the proper combination of block basis states for the total system described in a given $m_s = N_{\text{up}}^{\text{TOT}} - N_{\text{down}}^{\text{TOT}}$ spin sector. In a straightforward application of the DMRG method the first few eigenvalues of each m_s spin sector are determined and the classification of the singlet, triplet, quintet etc. levels can be accomplished based on the degeneracy of the levels. It is, however, often difficult to determine whether two close-lying energy calculated in two different m_s sectors are two components of the same level or not. This can be resolved by classifying the block states with respect to the irreducible representations of as many symmetry groups as possible in order to make use of their direct product in targeting the right quantum states.

In our present implementation we use apart from the particle number operator and the \hat{S}_z operator also the spin reflection operator, which enables us to separate the triplet manifold from the singlet manifold by targeting the states of appropriate parity of their spin part. Obvious extensions in future work would be the implementation of the point-group symmetry of the molecule and the \hat{S}^2 operator.

D. Dipole moment function

In the DMRG procedure the expectation value of the one electron operators can be calculated from the one-particle density matrix according to

$$\langle A \rangle = TR(\rho A), \quad (8)$$

where A is an N by N matrix of the operator for a first-order property, in the same one-particle basis that was used to construct the original T_{ij} and V_{ijkl} .

Once the target state was obtained, the one particle subsystem reduced density matrix ρ can be formed for any $B_L\bullet$ configuration as

$$\rho_{ij} = \langle \Psi_{\text{Target}} | \sum_{\sigma} c_{i\sigma}^{\dagger} c_{j\sigma} | \Psi_{\text{Target}} \rangle \quad (9)$$

where i, j denote sites in the left block. The one-particle density matrix for the right block is determined in a similar way. If i is in the left block and j in the right block, then ρ_{ij} is constructed from the one-particle operators of the two blocks.

E. Basis states

Comparing with the benchmark full-CI calculation of Bauschlicher and Langhoff [9] we have correlated six electrons of the LiF molecule by the QC-DMRG method on a chain built up from 25 CASSCF orbitals. The active space used to determine the latter contains two a_1 orbitals and no b_1, b_2 or a_2 orbitals. The MOLPRO program [23] was used to prepare the T_{ij} and V_{ijkl} matrix elements in this basis.

The Gaussian basis set used for lithium was derived from the (9s) primitive set of Huzinaga [24], supplemented by the (4p) functions optimized for the 2P state as in Ref. 25. The s and p primitives are contracted (5211) and (31), respectively. The F basis set is the Dunning [26] [4s2p] contraction of the Huzinaga [24] (9s5p) primitive set. To describe F^- , a diffuse 2p and a 3d polarization function are added; the exponents are 0.08 and 1.4, respectively.

F. Ordering molecular orbitals

It has become evident that the efficiency and accuracy of the QC-DMRG method depends strongly on the ordering of the orbitals [16, 17, 22]. Since this question is still an open field of research, we have repeated our previous calculations on H_2O , CH_2 and F_2 molecules in order to determine a strategy for the best ordering for LiF.

We have applied various algorithms which reorder the row and column indices of a sparse matrix in a way such that off-diagonal elements are moved closer to the diagonal or to one corner of the matrix. Extending the work of Chan and Head-Gordon [16], we have included a criterion based on the Fock operator as well as their originally proposed criterion based on T_{ij} . Thus we applied the re-ordering algorithms to the

$$F_{ij} = T_{ij} + \sum_{k \text{ occupied}} (4V_{ikkj} - 2V_{ikjk}) \quad (10)$$

matrix in order to include some components of the electron-electron interaction term as well. In the re-ordering process, we have neglected terms of F_{ij} below a certain threshold in order to pick up only the most important components. Of course, this procedure is useful only in the case of orbitals differing from Hartree-Fock orbitals, because for the latter F_{ij} is diagonal.

In agreement with the work of Chan and Head-Gordon we have found that a particularly satisfactory ordering can be achieved by using the Cuthill-McKee method [27, 28]. As a benchmark test, in case of F_2 molecule with $TRE_{max} = 10^{-10}$ and $M_{min} = 64$ parameter sets a 10^{-6} in absolute error of the ground state energy was reached with $M_{max} = 950$ –1100 states, in contrast to our previous results [17] when the same accuracy was reached with 1700–1800 block states. In addition, the number of sweeps was reduced by a factor of two. Similar results were found in the other test cases as well. Thus we can conclude that moving the off-diagonal elements closer to the diagonal with the Cuthill-McKee algorithm reduces the number of block states and accelerates the speed of convergence. It is worth to note, that this protocol is only expected to give good results if a mean-field description of the system is reasonable, i.e., in weakly correlated cases.

Based on our observations, we have applied the Cuthill-McKee method on the one-electron F_{ij} interaction matrix to determine the ordering configuration for

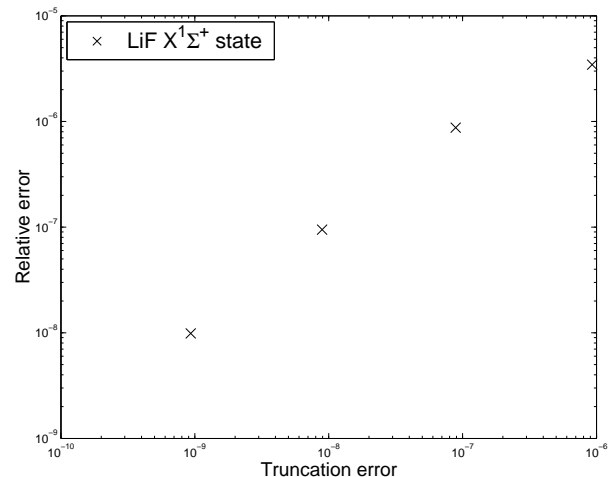


FIG. 2: Relative error of the ground state energy as a function of the truncation error.

LiF for all the different bond lengths. We have found the same ordering at both sides of the avoided crossing; the orbital ordering which we used in our calculations is detailed in Table I.

G. Controlling numerical accuracy

It has been shown in Ref. 17 that the accuracy of the QC-DMRG method can be controlled by method which we called dynamic block state selection (DBSS) approach, whereby the desired accuracy can be predetermined in advance of the calculations. Based on the Full-CI energies calculated at several points on the potential curve we can infer that the smallest value of the energy gap close to the avoided crossing is in the order of 10^{-3} , thus it is sufficient to obtain an accuracy of 10^{-4} in the absolute error of the energy levels. In case of the LiF molecule represented with the given basis states this means a relative error of 10^{-6} , thus the parameter that controls the maximum value of the truncation error has been set to 10^{-7} . For the minimum number of block states (M_{min}) a few hundred states would be sufficient.

We have made several test calculations with the above parameter set and found that the relative error indeed converged to 10^{-6} . As an example of the linear relationship between the relative error and the truncation error we have plotted our results obtained for various values of TRE_{max} parameter close to the avoided crossing ($R = 11.5$ a.u.) in Fig. 2.

On the other hand, in order to provide a better benchmark test, we have also used a smaller value of TRE_{max} for most of our calculations. We have set TRE_{max} to 10^{-9} which ensures an absolute error of 10^{-7} for the lowest energy state of a given m_s spin sector. The accuracy of the excited state energies, on the other hand, can depend strongly on other parameters and the construction of the target state which will be examined in detail in

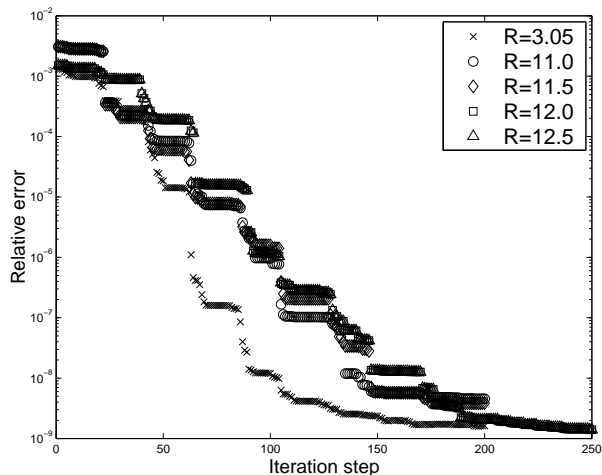


FIG. 3: The relative error of the ground state energies as a function of iteration steps at various bond lengths

the next section.

III. NUMERICAL RESULTS

We have carried out a detailed DMRG study of the absolute error of the ground and several excited state energies and the dipole moment as a function of bond length, focusing on the avoided crossing, where the wavefunction and also the convergence properties of DMRG is expected to change rapidly.

A. Ground state

According to our previous study [17] first we ran a calculation with $M_{min} = 164$ block states and repeated the same calculation with $M_{min} = 64$. We have found that using the Cuthill-McKee reordered orbital configuration the desired accuracy was achieved with the smaller M_{min} value as well, thus we have carried out all of our calculations with the latter value. This in fact sped up the calculation significantly reducing the computational time to an order of an hour on a standard PC running at 1.5 GHz.

We have found that the desired accuracy of the ground state was achieved for all bond lengths, even close to the avoided crossing. As an example we have plotted in Fig. 3 the relative error of the ground state energy as a function of the DMRG iteration steps at various bond lengths. It can be seen that the relative error of the ground state energy converges to 10^{-9} in all cases. The speed of convergence, however, is slower closer to the avoided crossing as expected because of the smaller gap and longer coherence length. We have also found that the largest numbers of the block states (M_{max}) generated dynamically fell in the range of 150–200 at the equilibrium point,

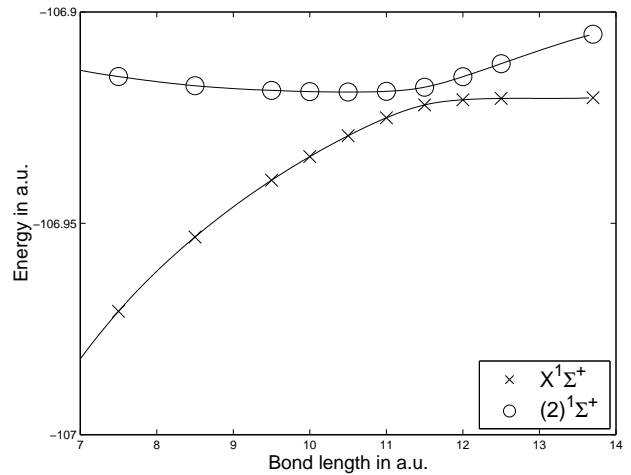


FIG. 4: The calculated potential curve in the vicinity of the avoided crossing. The DMRG results agree up to six digits with the Full CI results.

while it was slightly larger (400–500) close to the avoided crossing.

B. Excited states

In order to determine higher-lying excited states, we have used the spin flip operator to separate the singlet and triplet components. We have found that the first excited state ($^3\Pi$) is the lowest state of the even spin symmetry sector at small bond distances and exhibits the same convergence property as the ground state. Targeting the second level of the odd spin symmetry sector provided the $^1\Pi$ level at the equilibrium point at $R = 3.05$ up to six digits, as expected. We have also targeted higher-lying levels to obtain the second $^1\Sigma^+$ state, but the convergence of the method was much slower.

Targeting the second level of the even spin sector for increasing bond lengths, we have found that the target state can be lost when R is close to the avoided crossing. This is, in fact, not unexpected, and we made use of coherent and incoherent target states in order to resolve the problem. In addition, to provide better stability of DMRG it is advantageous to use larger values of M_{min} , thus we have set it to 200–300. Using the incoherent target states method, the $^1\Sigma^+$ state was also determined within an accuracy of 10^{-7} for all bond lengths. Our result for the obtained potential curve is plotted on Fig. 4, which agrees up to six digits with the Full-CI result, also given in Table II. Bauschlicher and Langhoff have pointed out that a careful selection of the CASSCF space used in the determination of the orbitals for the MRCI treatment is mandatory in order to get close agreement with FCI results. By contrast, we have found that routine methods for the determination of the orbital basis are adequate in our DMRG treatment. Indeed, Hartree-Fock orbitals yielded practically the same results, corroborat-

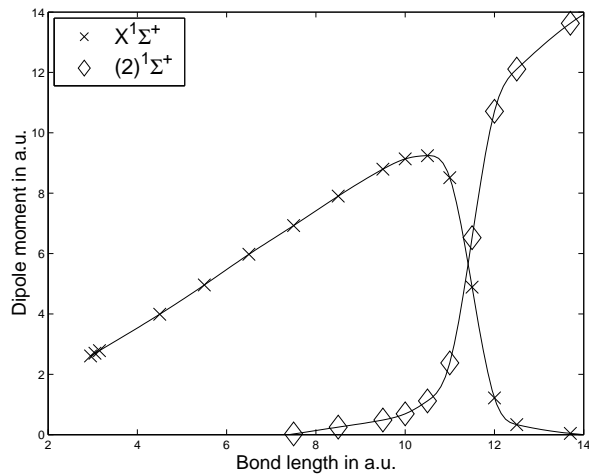


FIG. 5: The ground and excited states dipole moment as a functions of the bond length.

ing the view that DMRG treatments can be effectively converged to the Full CI result. We have also calculated the energy levels of the $m_s = \pm 1, 2$ sectors and found that the the residual splitting of the $m_s = 0, 1, -1$ components of the triplet level was as low as 10^{-10} a.u.

C. Dipole moment function

We have calculated the one-particle density matrix and the dipole moment for the various bond lengths. The dipole moment function is obtained as a smooth curve close to the Full-CI result. Note that especially the determination of the dipole moment curve in the vicinity of the avoided crossing proved very difficult in case of approximate methods of standard quantum chemistry. No special parameters are used in the DMRG calculation, i.e., it may be used as a ‘black box’ method, whereas considerable skill is required to choose the appropriate CASSCF parameters necessary to obtain satisfactory orbitals for an MRCI treatment. The absolute error of the dipole moment function was 10^{-5} at the equilibrium point and the largest error of the order of 10^{-3} was found at $R = 11.5$ a.u. Our results for the ground and excited states are shown in Fig. 5 and detailed in Table III.

D. The stability of structure of the wavefunction

Within the framework of the configuration interaction method the number of Slater determinants included in the treatment is increased systematically in order to achieve a better accuracy. Thus the wavefunction is improved by adding in turn single, double and higher excitations. On the other hand, the coupled cluster procedure includes higher excitations in a different fashion, adding excitations of a very limited kind (namely the

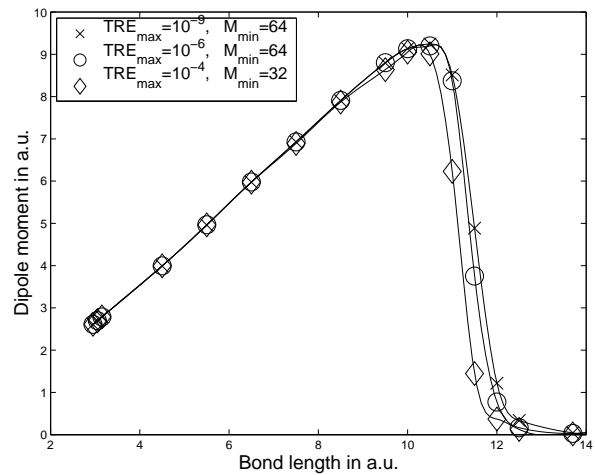


FIG. 6: The ground state dipole moment as a function of the bond length calculated for the different values of TRE_{max} parameter.

unlinked clusters) at a very early stage of approximation. By contrast, DMRG takes into account excitations even of higher excitation classes at the very beginning, picking up the most important ones by minimizing the energy. This means that if the accuracy of the calculation is lowered, the structure of the wave function is retained in essence. To demonstrate this, we have recalculated the ground state energies and the dipole moment with $TRE_{max} = 10^{-6}$ and found that the dipole moment function is still a continuous function even close to the avoided crossing. The relative error of the ground state energy was found to converge to 10^{-5} and the dipole moment to 10^{-4} at $R=11.5$ a.u. Repeating the same calculation by cutting the parameters drastically and using $M_{min} = 32$ and $TRE_{max} = 10^{-4}$, the dipole moment is still a continuous curve but it deviates more significantly from the FCI results especially close to the avoided crossing (Fig. 6). This simply means that some of the important components of the wave function are lost at the very beginning, which is of particular importance at the avoided crossing.

IV. SUMMARY

We have studied the low-lying energy spectrum of LiF molecule by the quantum chemistry version of DMRG in order to demonstrate the efficiency of the method in the vicinity of an avoided crossing. Besides calculating the ground and several excited states energies, we have obtained the dipole moment function as well. Several technical aspects of the QC-DMRG method were further studied. We have extended the application of the dynamic block state approach and the study of optimal ordering configuration of molecular orbitals.

We have found that reordering the molecular orbitals with the Cuthill-McKee algorithm applied on the T_{ij} ma-

12	11	10	9	8	7	6	5	4	3	1	2	18	17	16	15	13	14	24	23	22	21	19	20	25
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TABLE I: Orbital ordering employed in this work

R	DMRG	DMRG	FCI	FCI
a.u.	E_{GS}	$E_{(2)^1\Sigma+}$	E_{GS}	$E_{(2)^1\Sigma+}$
2.95	-107.111724	-106.797843	-107.111726	-106.797846
3.05	-107.113052	-106.806390	-107.113055	-106.806392
5.50	-107.024654	-106.873564	-107.024656	-106.873565
6.50	-106.994852	-106.892601	-106.994853	-106.892602
7.50	-106.970816	-106.915277	-106.970817	-106.915277
8.50	-106.953232	-106.917457	-106.953232	-106.917457
9.50	-106.939803	-106.918556	-106.939803	-106.918556
10.00	-106.934216	-106.918837	-106.934216	-106.918838
10.50	-106.929276	-106.918948	-106.929277	-106.918948
11.00	-106.925037	-106.918782	-106.925037	-106.918782
11.50	-106.921985	-106.917803	-106.921985	-106.917804
12.00	-106.920778	-106.915314	-106.920779	-106.915314
12.50	-106.920455	-106.912236	-106.920455	-106.912239
13.70	-106.920295	-106.905273	-106.920295	-106.905274

TABLE II: The ground and first excited state energies in atomic units as functions of bond length.

trix elements or the Fock matrix the same accuracy compared to an ordering based on the orbital energy can be achieved with a smaller minimum number of block states (M_{min}). The QC-DMRG procedure selects out a significantly smaller number of block states, M_{max} , and the number of iteration steps is reduced. In addition, we have shown the efficiency and stability of the dynamic block state selection approach which in fact reduces the computational time significantly.

It turns out that the desired accuracy of the lowest states of each spin symmetry sector can be achieved for all bond lengths by targeting that particular state. On the other hand, calculating higher-lying levels close to the avoided crossing, coherent or incoherent superpositions of target states have to be constructed in order to provide stability and convergence. Since this has no significant effect on calculations far away from the avoided crossing where the energy gap is large, this method can be used for the whole range of bond lengths.

The dipole moment calculated by DMRG can also be determined with good accuracy for all bond lengths and in fact it is a continuous curve even close to the avoided crossing. We have found that adjusting the desired accuracy of the calculation affects the accuracy the dipole moment, but the dipole moment function remains a con-

tinuous curve. This demonstrates the power of DMRG in quantum chemistry, since the structure of wavefunction does not change significantly for lower accuracy, namely the most important configurations are picked up even with lower accuracy.

As far as the technical questions are considered, using reordered orbitals and the DBSS approach QC-DMRG calculation time was found to be within the order of magnitude of the FCI calculation if point-group symmetries are not used. Although the point group symmetry is not built in our present implementation of the DMRG method, the structure of the V_{ijkl} matrix reflects the symmetry, and the number of nonzero matrix elements is reduced significantly.

Acknowledgments

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R	DMRG	DMRG	FCI	FCI
a.u.	μ_{GS}	$\mu_{(2)^1\Sigma^+}$	μ_{GS}	$\mu_{(2)^1\Sigma^+}$
2.95	2.609571	-0.461813	2.609585	-0.461810
3.05	2.697383	-0.462597	2.697402	-0.462597
5.50	4.959323	-0.528943	4.959400	-0.528936
6.50	5.975189	-0.161147	5.975169	-0.161177
7.50	6.926324	0.024134	6.926329	0.024112
8.50	7.903448	0.250507	7.903463	0.250889
9.50	8.795699	0.485936	8.795784	0.485905
10.00	9.136214	0.689593	9.136292	0.689562
10.50	9.243327	1.117497	9.243389	1.117521
11.00	8.513409	2.375437	8.513886	2.376136
11.50	4.886492	6.524977	4.889316	6.523027
12.00	1.218095	10.711791	1.218455	10.711489
12.50	0.333931	12.110902	0.334032	12.110658
13.70	0.042024	13.628204	0.042074	13.628195

TABLE III: The ground and first excited state dipole moments in atomic units as functions of bond length.

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